To Scott R. 6 May 82

UNITED STATES ENVIRONMENTAL PROTECT AGENCY

DATE April 23, 1982

SUBJECT: Spring River Fish

Site: Syntex Verona JDB
ID # MOD007452154
Break: 3.3
Other: EPA
4-23-82
0751

FROM: Robert D. Kleopfer, Ph.D. RDK
Chief, Organic Analysis Section, LABO/ENSV

TO: Daniel J. Harris
EP&R/ENSV

As described in my memo of March 25, 1982, it was arranged to have two Spring River fish extracts analyzed by negative ion atmospheric pressure mass spectrometry (NIAPI-MS) at the National Center for Toxicological Research (NCTR). The results of those analyses are attached and a summary follows:

2,3,7,8-TCDD RESULTS IN PPT (DETECTION LIMIT)

SAMPLE NUMBER	CNFRL	UNL	NCTR
AA2406-(1 thru 5)	N.D. (1)	N.D. (9)	N.D. (25)
AA2405-(1 thru 6)	37	52	55

The University of Nebraska - Lincoln (UNL) lab also reported the presence of other TCDD isomers in sample AA2405 (58 PPT of an isomer eluting after 2,3,7,8-TCDD). The NCTR results indicate that this late eluting isomer does not have the 2:2 substitution pattern. Thus, the number of possible isomers has been reduced to 8 for the unidentified TCDD isomer. Retention order data reported by Buser and Rappe (ANAL. CHEM. 1980, 52, 2257-2262) indicates that the isomer reported by UNL is 1,2,3,9-TCDD.

Structure - activity relationships suggest that this isomer is relatively non-toxic. However, the NIAPI-MS technique indicated the presence of at least two other PCDD's (one trichloro and one pentachloro isomer) at levels estimated to be 40 PPT for each.

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SUPERFUND RECORDS

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
FOOD AND DRUG ADMINISTRATION

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NATIONAL CENTER
FOR TOXICOLOGICAL RESEARCH
JEFFERSON, ARKANSAS 72079

4/8/82

Robert D. Kleopfer, Ph.D.
EPA
25 Funston
Kansas City, Kansas 66115

Dear Dr. Kleopfer:

Enclosed is your copy of our report on the two fish extracts sent to us from UNL. We hope this information will be useful to you. We are glad to be able to be of assistance to the EPA.

Sincerely,

Walter A. Korfmacher

Walter A. Korfmacher, Ph.D.
Chemist

enclosure
WAK/bj

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4/8/82

Lal Weerasinghe, Ph.D.
Department of Chemistry
University of Nebraska-Lincoln (UNL)
Lincoln, NE 68588

Dear Dr. Weerasinghe:

On Friday, April 4, I received the two fish extract samples that you sent to me. These were analyzed by our GC/NIAPI/MS system on 4/5/82 and 4/6/82. The results of our analyses are summarized below.

2,3,7,8-TCDD

Sample "A": 54.8 ± 19.3* ppt (pg/g)
Sample "B": None Detected (detection limit 25 ppt)
(*95% confidence limits)

NOTE: These results are based on the inclusion by the UNL lab of 250.0 ppt of 2,3,7,8-TCDD-^{13}C in the extracts. It was assumed that the isotopic distribution of the UNL 2,3,7,8-TCDD-^{13}C is similar to our 2,3,7,8-TCDD-^{13}C upon which our calibration curve is based. The isotopic distribution of our 2,3,7,8-TCDD-^{13}C is 78.4% $^{13}C_{12}$, 17.4% $^{13}C_{11}$ and 4.2% $^{13}C_{10}$. If the UNL 2,3,7,8-TCDD has a significantly different percent of $^{13}C_{12}$ then our quantitative results need to be adjusted accordingly.

Other TCDD isomers:

Sample "A": No other TCDD isomers detected
Sample "B": No other TCDD isomers detected

We have enclosed copies of the computer reports for 2,3,7,8-TCDD for each of these two samples. In addition, we have enclosed a copy of our recently published paper which describes our isomer-specific method for 2,3,7,8-TCDD.

We hope this information will be useful to you and to the EPA. We will be glad to cooperate with you in the future on other samples in which you may have a question.

Sincerely,

Walter A. Korfmacher, Ph.D.
Chemist

enclosures
WK/bj
cc: R.D. Kleopfer, Ph.D., EPA, Kansas City
R.K. Mitchum, Ph.D., NCTR, HFT-154
D.L. Stalling, Ph.D., CNFRL

NOTE: Our GC/NIAPI/MS method will only detect 2:2 TCDD isomers.

Other PCDD isomers:

Sample "A": Two peaks were detected, one may be a 1:2 Tri-CDD and the other may be a 2:3 Penta-CDD (see note)

Sample "B": No other peaks were detected

NOTE: In sample "A", two peaks were noted in the analysis of the extract. One peak was at RRT = 0.802 (relative to 2,3,7,8-TCDD), the other was at RRT = 1.16. We have analyzed all 22 TCDD isomers, and they occur, on our column and conditions, in a window from RRT = 0.813 to 1.10. Thus, we know that these peaks are not TCDDs. But, they were detected on our GC/NIAPI/MS system as real peaks at both m/z 176 and 178. In addition, these peaks had acceptable 176/178 area ratios so that they are most likely due to dichloro-1,2-benzoquinone radical ions.

If we wish to speculate on what these peaks may be formed from, we would proceed as follows. Recent experimental studies in our laboratory have suggested that PCDDs other than TCDDs may also fragment in a manner analogous to our well-documented TCDD-O_2 reaction under NIAPI conditions. While we have no direct experimental evidence of this speculation, it may be that 2:3 Penta-CDDs and 1:2 Tri-CDDs would produce ions at m/z 176 and 178 in our system. If this is correct, then we can speculate that considering the GC retention times, the peak at RRT = 0.802 is due to a 1:2 Tri-CDD and the peak at RRT = 1.16 is a 2:3 Penta-CDD. A very rough estimate can be made of the quantitative levels of these PCDDs by treating them as if they were 2,3,7,8-TCDD and comparing their m/z 176 peak area to the 2,3,7,8-TCDD-^{13}C peak area. If this calculation is performed, the resulting estimate for each of these peaks is about 40 ppt.